

Crystallization of Hydrosodalite $\text{Na}_6[\text{AlSiO}_4]_6(\text{H}_2\text{O})_8$ and Tetrahydroborate Sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{BH}_4)_2$ inside the Openings of Wafer-Thin Steel Mesh

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Abstract

The zeolitic properties of hydrosodalite $\text{Na}_6[\text{AlSiO}_4]_6(\text{H}_2\text{O})_8$ and the reactivity and hydrogen content of tetrahydroborate sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{BH}_4)_2$ favour both species for future industrial applications. A use in chemical process often efforts a sample preparation in form of membrane-like thin wafers. The present study presents experiments on hydrosodalite as well as BH_4 -sodalite formation as steel mesh supported thin wafers. Preparation of both sodalite wafers is performed by the crossover synthesis (CS) from solution to melt flow, first described in [1] [2]. Whereas the space filling of the steel mesh with BH_4 -sodalite crystals was proved to be a complete close and stable package, hydrosodalite reached only a somewhat weaker quality. Beside the synthesis step, hydrosodalite formation requires a treatment of the crystal filled mesh at 130°C for 20 h in water to transform the as synthesized hydroxysodalite into hydrosodalite, as known from literature [3] [4] [5]. This leaching procedure was found to be responsible for the obtained loss of quality as demonstrated by a further experiment using a self supported hydrosodalite wafer. Further problems like evolution of pores as a result of the mechanically ripping out the steel inlay from the sample pellets after synthesis have to be solved in future. Nevertheless the results of the present paper are of significance for the development of steel mesh supported hydrosodalite and BH_4 -sodalite membranes.

Keywords

Microporous Materials, Chemical Synthesis, Steel Mesh Supported Membranes, BH_4 -Sodalite, Hydrosodalite

1. Introduction

Hydrosodalites $\text{Na}_6[\text{AlSiO}_4]_6(\text{H}_2\text{O})_8$ and tetrahydroborate-sodalites $\text{Na}_8[\text{AlSiO}_4]_6(\text{BH}_4)_2$ are of great interest for future applications. Hydrosodalite is the only member of the sodalite family with zeolitic properties [6]. Borate sodalite contains BH_4 groups and preserves these reactive species over years within the sodalite cages [7] [8]. The zeolitic properties of hydrosodalite and the reactivity and hydrogen content of BH_4 sodalite favours both materials for utilization in industry but a use in chemical process often efforts a sample preparation in form of thin membrane-like wafers. Crystallization techniques to form dense agglomerated crystalline aggregates and intergrowth's of sodalites are therefore suitable. In the field of sodalite synthesis, common hydrothermal process of alkaline transformation of kaolinite is revealed as the most preferred method but only formation of fine powder instead of dense agglomerates results therefrom [4] [9] [10]. But recently upgraded synthesis procedures were developed mainly as model systems but also with particular potential for future utilization in industrial process. Solvent free synthesis of zeolites [11] [12] [13] and other compounds [12] [13] [14] [15] [16] is one route for insertion of modified reaction conditions. Other interesting new methods are the autothermal synthesis, where the whole process energy is allocated by the enthalpy of a tailored reaction system itself [17] as well as the crossover synthesis from gel to melt flow [1] [2].

The present study uses the new method first demonstrated in [1] where halide-, borate and nitrite sodalites as well as BH_4 -sodalite [2] have been obtained by crystallization of a dense pressed pellet of solid educts. The procedure is a one-pot process under open conditions. This so-called "crossover synthesis (CS)" starting with crystallization in (aqueous) gel-like solution and crossover into crystal growth in melt (flux) based upon two distinctive features, both ruled by controlled heating of a suitable mixture of reagents. Firstly the nucleation and early growth step proceeds within the reagents own hydrate water released during heating, *i.e.* under conditions related to a mild hydrothermal process. Secondly further crystal growth occurs by a shift of the conditions to a melt flux reaction at elevated temperature with NaOH as the suitable flux component, already added to the educts.

The present work demonstrates this new preparation technique as a case study to synthesize steel mesh supported hydrosodalite and BH_4 -sodalite thin wafers.

Hydroxysodalite membranes were already tested for the separation of small molecules (water, hydrogen or helium) [18]-[25]. In contrast hydrosodalite membranes will become more and more important in future as an increase of the separation efficiency is highly expected from their strong zeolitic properties, compared with hydroxysodalite.

The present investigation starts with synthesis experiments of hydrosodalite and BH_4 -sodalite on stainless steel nettings of 20 μm mesh aperture under CS conditions. Whereas BH_4 -sodalite can be prepared in a one step process, hydrosodalite formation as single phase product requires a second step of hy-

drothermal leaching in water at 130 °C for 20 h, known from literature on transformation of polycrystalline powder of hydroxysodalite, obtained by mild hydrothermal process [3] [4] [5].

The influence of this strong leaching step was investigated in more detail under insertion of an as synthesized pellet of hydroxysodalite without a steel mesh inlet to characterize possible damage on surface and inside the pellet. This investigation is of importance to decide, if a self supported thin wafer of hydrosodalite can be produced.

All samples were analysed by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

The results of the present paper are of significance for future improvement of wire mesh and self supported sodalite membranes.

2. Experimental

The experimental conditions are summarized in **Table 1**. Experiments No. 1 and 2 were performed to investigate sodalite synthesis on steel mesh under CS conditions. In both experiments zeolite 13-X $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$ (Fluka 69856) was selected as a suitable reactant for controlled thermal reaction as recently demonstrated in [1] [2]. Besides the role as Al-Si-source the function of Zeolite 13-X as “water provider” in the gel step of the crossover reaction is of main importance here. The following preparation procedure developed in [1] [2], was inserted in the present study too: 200 mg zeolite 13-X and 50 mg NaOH granulate (Merck 1.06467) and in the case of BH_4 -sodalite 200 mg of NaBH_4 (Merck 806373) were mixed and pressed with 50 kN for 5 minutes into a pellet of 13 mm diameter and 1.25 mm thickness. A circular stainless steel net of 20 μm mesh aperture and 9 mm diameter was inserted within the powder mixture before pressing. The steel net was cleaned with acetone, washed with water and once dipped into a 16 M NaOH solution, before its use. A controlled heating

Table 1. Experimental conditions and products.

Syntheses of sodalites on steel mesh						
Exp. No.	Reactants (mg)	Preparation parameters			Product according XRD and FTIR	Cell parameter (Å)
		Synthesis method*	Temperature(°C)/time (h)	Washing procedure/ml H ₂ O		
1	13X + NaOH (200 + 50)	CS + leaching	400/4	Hydrothermal leaching of wire netting (40)	Hydrosodalite	8.849 (2)
2	13X + NaOH (200 + 50) + NaBH_4 (200)	CS	350/4	Washing of wire netting (150)	NaBH_4 -sodalite	8.910 (1)
Synthesis of hydrosodalite as self supported thin mould						
3	13X + NaOH (200 + 50)	CS + leaching		Hydrothermal leaching of the whole product pellet (40)	Hydrosodalite + zeolite P	8.854 (1)

*CS: crossover synthesis (heating of a solid educt pellet under open conditions, see text).

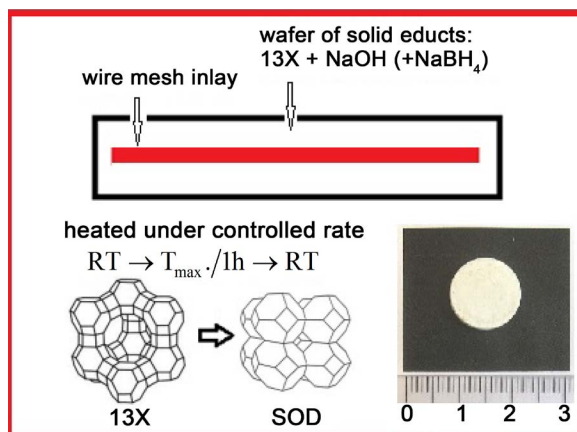


Figure 1. Schematic view of the experimental procedure of CS process and the reactants pellet (scale in cm; thickness of the pellet is 1.25 mm).

process of the pellets was performed under open conditions in a Pt-crucible. A heating program $RT \rightarrow T_{max.} \rightarrow RT$ (hydrosodalite: $T_{max.} = 400^{\circ}C$; BH_4 -sodalite: $T_{max.} = 350^{\circ}C$) was revealed for syntheses with 90 min. heating up time, a 60 min. holding period at $T_{max.}$ as well as a 90 min. cooling step. **Figure 1** gives a schematic view of the experimental CS procedure. An image of the reactants pellet is included in this Figure (13 mm diameter and 1.25 mm thickness).

After the heating procedure the crystal filled steel mesh was ripped out of the pellet with a cutter. The BH_4 -sodalite synthesis was completed after washing and drying the net. Hydrosodalite formation requires a second preparation step, as the as synthesized sodalite is hydroxysodalite that must be transformed into hydrosodalite by a hydrothermal treatment of the crystal filled net at $130^{\circ}C$ for 20 h in water as known from literature on hydroxysodalite powder, obtained by common hydrothermal synthesis [3] [4] [5]. After the leaching procedure the net was dried.

A further experiment (No. 3) was performed to investigate the influence of this strong leaching step in more detail. Therefore an as synthesized sample pellet without steel inlay was synthesized under the same conditions, already mentioned for the hydrosodalite sample No. 1. The investigation of the hydrosodalite transformation under insertion of the as synthesized pellet of hydroxysodalite without a steel mesh inlet is of importance to characterize possible damage of the crystal intergrowth on the surface and inside the pellet. This experiment is of special interest to decide, if a self supported thin wafer of hydrosodalite can be produced.

All samples were than analysed by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

X-ray powder patterns were measured in the $5^{\circ} - 80^{\circ}$ range of two Theta (step width 0.02° , 2 sec measuring time per step) on a Philips PW-1800 diffractometer (Bragg-Brentano geometry, $CuK\alpha$ radiation, secondary graphite monochromator). Data were evaluated using the WinXPow software (STOE).

A Vertex 80v FTIR spectrometer (Bruker AXS) was available to measure the in-

frared spectra of the products in the mid infrared region. The KBr wafer technique was therefore inserted under use of 1 - 2 mg sample powder and 200 mg KBr.

SEM analysis of the products was performed on a JEOL JSM-6390A at 30 kV acceleration voltage.

3. Results

Synthesis of hydrosodalite and BH_4 -sodalite on steel mesh (No. 1-2, Table 1)

The results of XRD analyses of the products are included in Table 1 and the X-ray powder patterns of the samples are summarized in Figure 2. The pattern of the 13X zeolite is inserted for comparison. From this Figure it can be seen that sodalites were obtained by the crossover synthesis in experiments No. 1 and No. 2 as pure phase products and in sufficient crystallinity.

Further valuable information on the sodalite structure as well as on the species, enclathrated within the sodalite cages can be derived from FTIR spectroscopy. Especially the detection of the $(H_2O)_4$ -cage fillings of hydrosodalite and of the BH_4 -anions in BH_4 -sodalite are very important in the present study to decide, if the leaching procedure from hydroxysodalite to hydrosodalite was complete or not and to control BH_4 -enclathration in BH_4 -sodalite.

Figure 3 gives a summary of the FTIR investigation of the products No. 1 (hydrosodalite) and No. 2 (BH_4 -sodalite); sample No. 3 is discussed below. A spectrum of the educt "zeolite 13X" is included in Figure 3 for further discussion and comparison.

The typical vibrations of the sodalite framework can be seen in the spectra of the sodalites. Beside a strong broad band of asymmetric T-O-T stretching vibra-

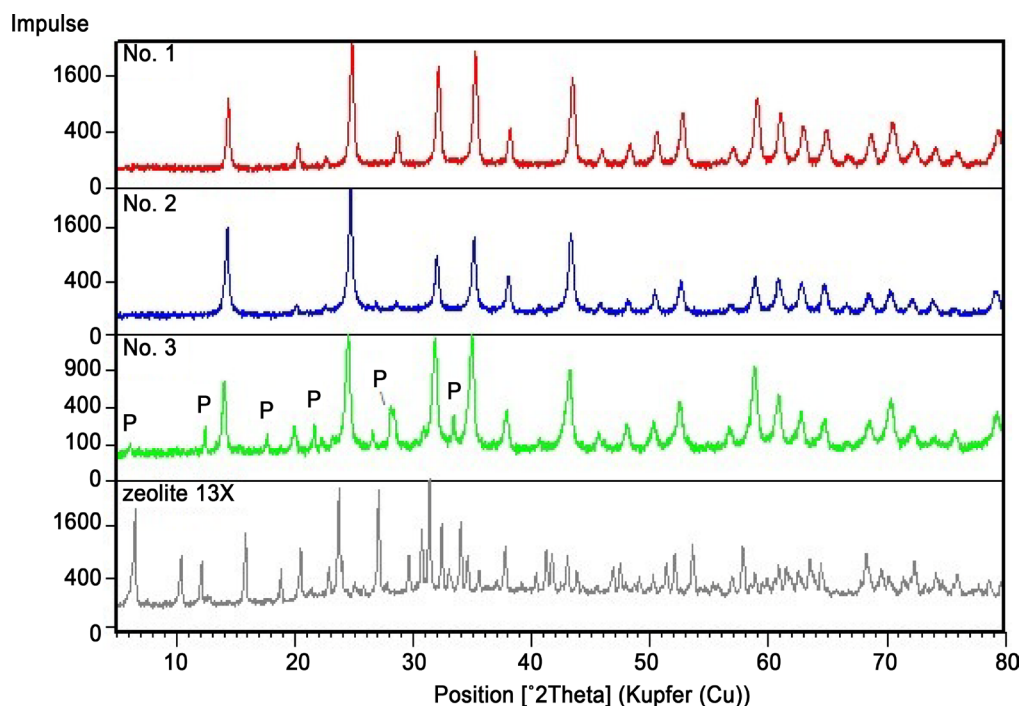


Figure 2. X-ray powder patterns of the products No. 1-3; byproducts in the sample No. 3: zeolite P (see text). The pattern of the 13X zeolite is inserted for comparison.

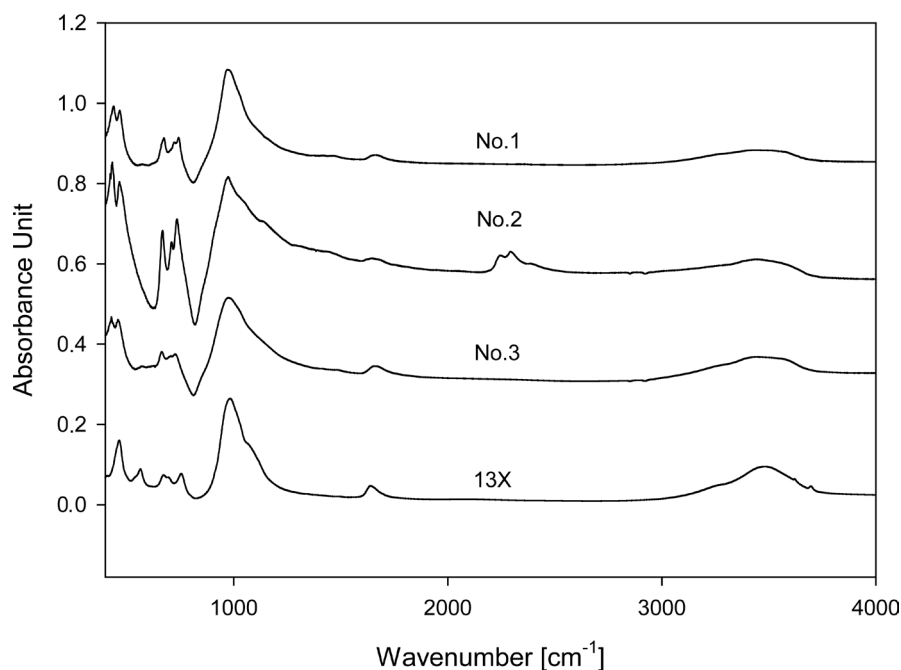
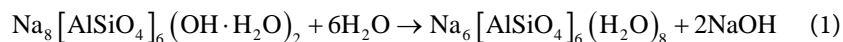


Figure 3. FTIR spectra of products No. 1-3, **Table 1**. The spectrum of zeolite 13X is inserted for comparison.

tions (T = Si, Al) around 1000 cm^{-1} , the symmetric T-O-T vibration modes (triplet in the $660\text{ cm}^{-1} - 740\text{ cm}^{-1}$ region) and the two intense bending modes at around 460 cm^{-1} and 430 cm^{-1} can be distinguished in accordance with literature [26]. In contrast, the educt zeolite 13X exhibits another typical “fingerprint”. The sodalite products are pure phase samples as no zeolite 13X vibration occur in their spectra. This is a clear sign for the total decomposition of zeolite 13X structure consistently with X-ray diffraction.

The formation of hydrosodalite can also expressively followed by the spectrum of sample No. 1. The spectrum exclusively exhibits the strong water bands at 1650 cm^{-1} and $3100\text{ cm}^{-1} - 3700\text{ cm}^{-1}$ but no vibration of O-H at 3640 cm^{-1} [27]. The leaching procedure of this sample proceeded quantitatively according to the reaction [3] [4] [5]:



The extent of the reaction (1) can also be followed by XRD, where the transition from hydroxysodalite to hydrosodalite yields to the typical contraction of the unit cell parameter from 8.89 \AA of hydroxysodalite to 8.85 \AA for hydrosodalite [3].

The spectrum of BH_4 -sodalite exhibits clear resolved framework vibrations of the sodalite network. The vibrations of BH_4^- anions at $1143(\nu_4)$, $2286(2 * \nu_4)$, $2241(\nu_3)$ and $2390(\nu_2 + \nu_4)$ can be clearly observed in accordance with literature data [28] [29] [30] [31]. Beside BH_4 some cage water and/or slightly adsorbed external surface water can be seen (bands at 1650 cm^{-1} and $3100\text{ cm}^{-1} - 3700\text{ cm}^{-1}$) [27]. A few impurities of carbonate from the starting educt mixture also occur within sample No. 2 (weak vibrations in the $1410\text{ cm}^{-1} - 1450\text{ cm}^{-1}$ region

of the FTIR spectrum [27]).

Figure 4 shows SEM images of the hydrosodalite-filled steel mesh sample of experiment No. 1 (**Table 1**) at different magnification. An average crystal size around $1.0\ \mu\text{m}$ is observed and the synthesis product is a mixture of fewer agglomerated more flaky crystals beside many separated spheroidal crystals. The typical dodecahedral form of sodalites from common hydrothermal synthesis is not developed here. The flaky habit and the strong intergrowth of sodalite crystals is typical for the CS synthesis method [1] [2]. This special feature of the method is the important requirement for stable fillings of the steel mesh cavities. The space filling of the mesh is complete but a very close package was not reached. Even some damage is observed due to the mechanically ripping out the steel inlay from the sample pellet after synthesis. Nevertheless the fillings are stable according to an indenting effect of the more platy crystals and the whole amount of crystals seems to be glued together. The strong hydrothermal leaching procedure of transformation of the hydroxysodalite into hydrosodalite seems to have a remarkable influence of the texture and packing density of the

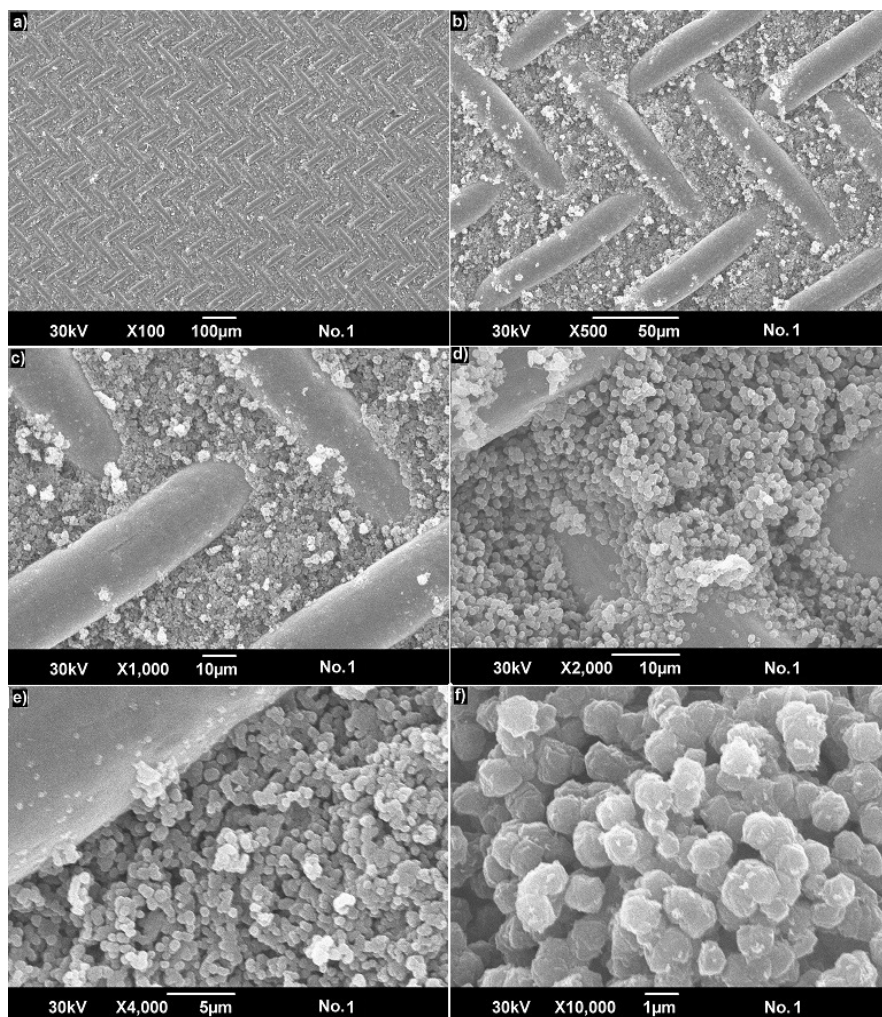


Figure 4. SEM images of the wire mesh supported hydrosodalite product No. 1 (**Table 1**) at different magnification.

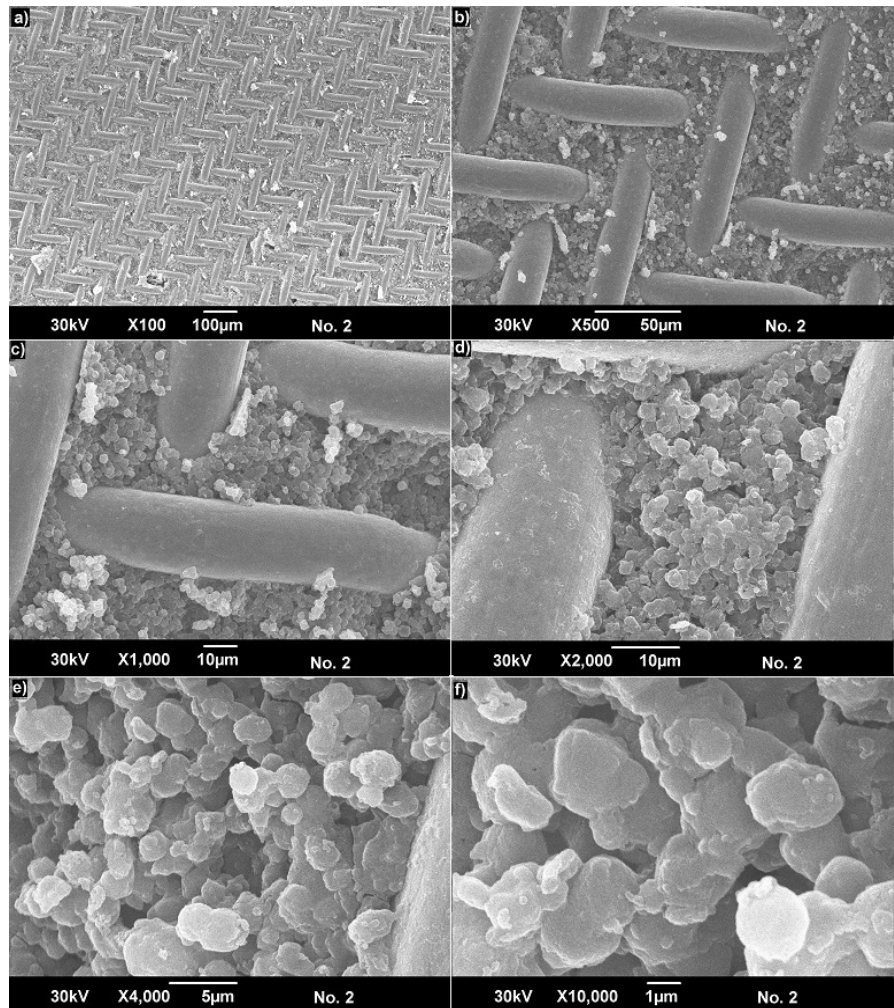


Figure 5. SEM images of the wire mesh supported BH_4 -sodalite (product No. 2, **Table 1**) at different magnification.

crystals. This will be discussed below for the case of sample No. 3.

Figure 5 shows SEM images of the BH_4 -sodalite filled steel mesh sample of experiment No. 2 (**Table 1**) at different magnification. An average crystal size around $1.5 \mu\text{m}$ can be estimated. Beside the larger crystals even the package density and correspondingly the mesh filling of the wire netting is better, compared with the hydrosodalite sample No. 1 (**Figure 4**). The BH_4 -sodalites occur as an agglomeration of flaky crystals. Even here the typical dodecahedral form of sodalites from common hydrothermal synthesis is not developed. Beside some damage due to the mechanically ripping out the steel inlay from the sample pellet after synthesis the mesh filling is sufficient and shows a close and stable package. The structure directing effect of BH_4 -anions for the sodalite structure type and the circumstance that no leaching procedure is needed to obtain BH_4 -sodalite seem to be the reasons for the better results compared with hydrosodalite sample.

Investigation of the influence of the leaching procedure—characterization of hydrosodalite in the as synthesized pellet form as self supported mould (experi-

ment No. 3, **Table 1**)

A further experiment (No. 3) was performed to investigate the influence of the strong leaching step of hydrosodalite formation in more detail. Therefore an as synthesized sample pellet without steel inlay was synthesized under the same conditions, already mentioned for the hydrosodalite sample No. 1. The investigation of the hydrosodalite transformation under insertion of the as synthesized pellet of hydroxysodalite without a steel mesh inlet is of importance to characterize possible damage of the crystal intergrowth on the surface and inside the pellet. This experiment is of special interest to decide, if a self supported membrane-like mould of hydrosodalite can be produced in future.

The sample was analysed by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

The result of XRD analyses of the product No. 3 is included in **Table 1** and the X-ray powder pattern of the sample is inserted in **Figure 2**. As for sample No. 1 it can be seen that sodalite was formed but now with an impurity of zeolite P (PDF No. 44-103 [32]). It is assumed that some amorphous parts within the as synthesized sample crystallized during the hydrothermal leaching process.

The FTIR spectrum of the sample exhibits close resemblance with the spectrum of hydrosodalite No. 1. The few amounts of the byproduct zeolite P are responsible for broadening of the asymmetric T-O-T vibration and very weak additional bands in the region of the symmetric T-O-T modes of sodalite.

In the present paper first the as synthesized pellet was investigated by SEM, before the hydrosodalite transformation was performed by leaching the whole as synthesized dense pellet with water at 130°C for 20 h in an autoclave. Without the leaching step the sample exhibits the character of hydroxysodalite. As the cages of hydroxysodalite are blocked by hydroxyl groups this sodalite shows a clathralite-like behaviour [33] and an insertion for instance for water separation seems to be restricted and is assumed to be more a result of grain boundary diffusion than inter-cage diffusion. In contrast hydrosodalite $\text{Na}_6[\text{AlSiO}_4]_6 \cdot (\text{H}_2\text{O})_8$ shows typical zeolitic sorption properties as already mentioned in the introduction. Exclusively hydrosodalite should be optimal for insertion of separation of small molecules from gases or liquids by adsorption, permeation or pervaporation. A cheap preparation of hydrosodalite membrane-like moulds by an optimized leaching procedure in connection with CR synthesis would be an important step for future industrial applications.

Figure 6 shows SEM images of the hydroxysodalite pellet *i.e.* of the sample No. 3 after CS but before the leaching procedure. The surface (left column) and the cross section according to sample separation by cutting with a lancet (right column) were analysed by SEM. A slightly rough surface can be derived at high magnification (images on left column of **Figure 6**). Pores and knuckle-like defects are distributed around the surface. In contrast the images of the cross section of the pellet surprisingly offer a very dense structure (right columns of **Figure 6**) and the pores and knuckles, observed on the surface, are not influencing the dense inner structure of the pellet. According to the compact thickness

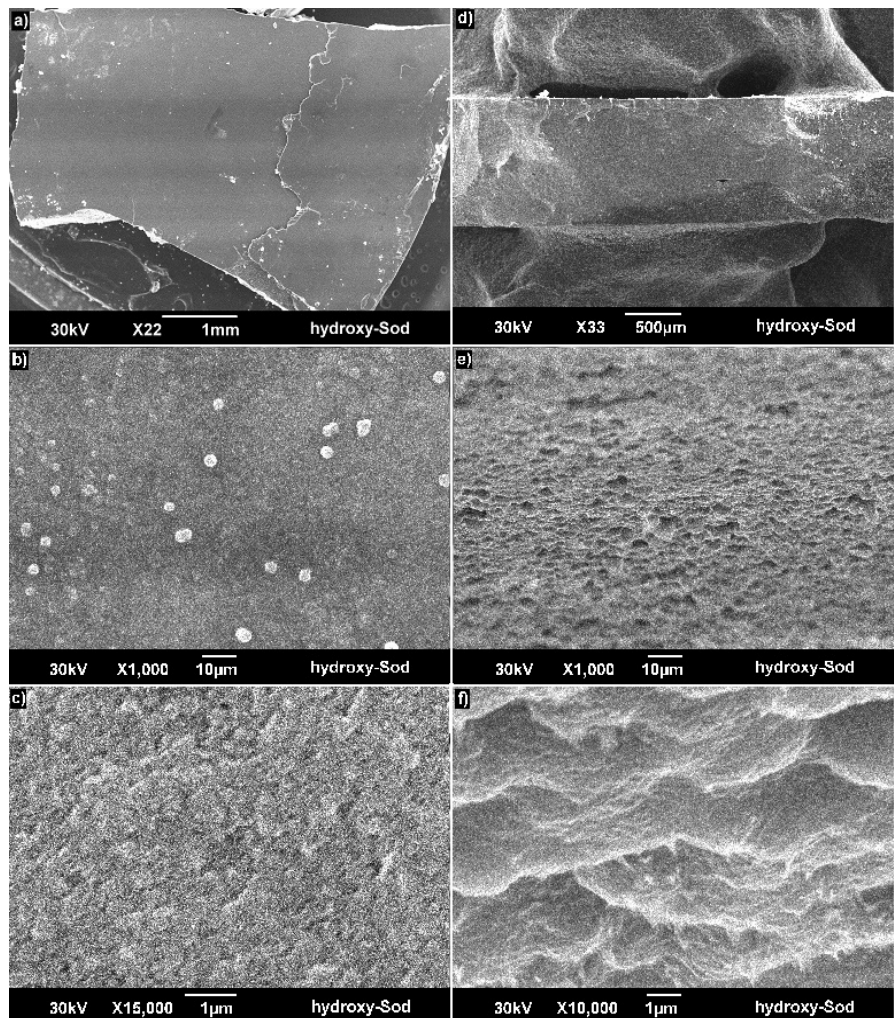


Figure 6. SEM images of the hydroxysodalite pellet of experiment No. 3 (**Table 1**) before the leaching process (left column: surface, right column: cross section).

of the sample of 1.25 mm (see **Figure 6(f)**) the surface pores and defects are not reaching a deeper volume of the sample and a connection of defects in the sense of a channel system can be excluded. A membrane-like character can be attributed to this hydroxysodalite mould.

Figure 7 gives a summary of SEM images of the hydrosodalite mould surface and its cross section (again prepared by cutting) of sample No.3, **Table 1** after the leaching procedure at 130°C for 20 h in water. According to this strong hydrothermal leaching process more or less larger pores were observed but according to the compact thickness of the membrane of 1.25 mm (see **Figure 7(d)**) the pores seem to exhibit a more separate character than a connected channel system and the mould maybe remains densely. But nevertheless it is assumed that these observed damages of the sample texture exclude a use as hydrosodalite membrane up to now. A further improvement of the hydrosodalite mould is necessary for a future insertion. Investigations of influence of pressure and time during pellet preparation and further optimization of heating parameters and leaching conditions after CR synthesis have to be performed in forthcoming studies.

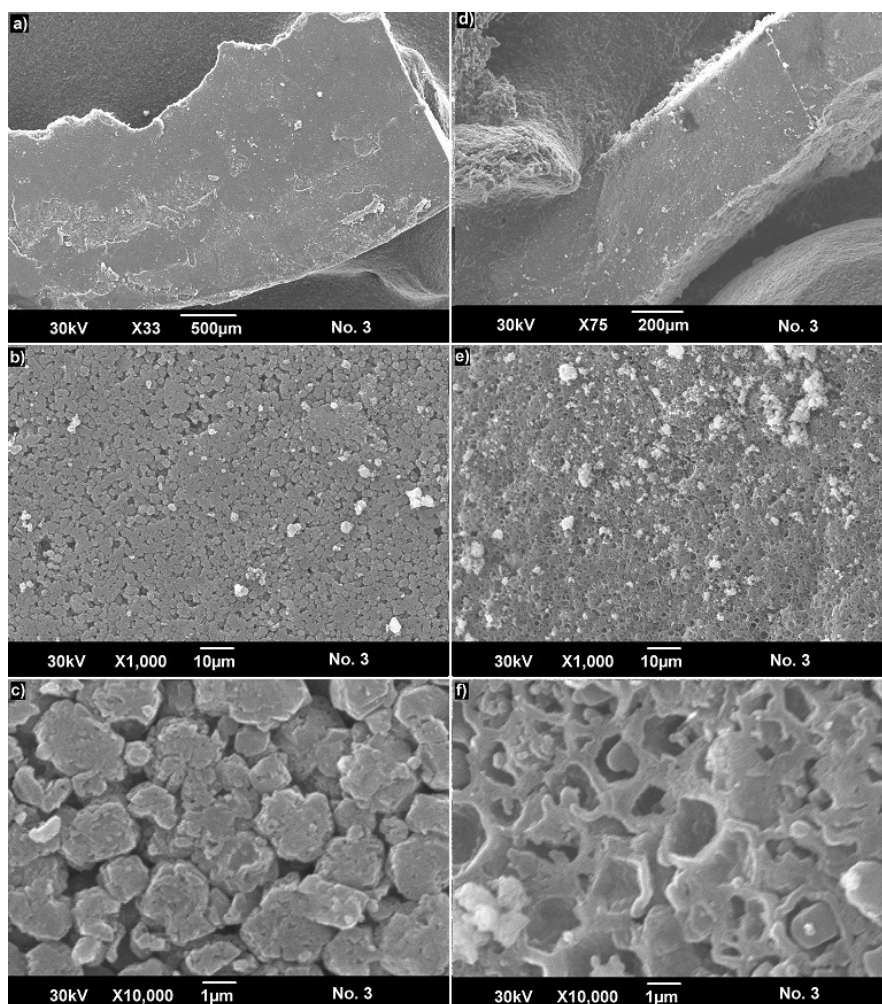


Figure 7. SEM images of the hydrosodalite pellet after leaching (experiment No. 3, **Table 1**, No. 3 a-c surface and No. 3 d-f: cross section).

4. Conclusions

The the crossover synthesis (CS) from gel-like solution to melt flow offers new possibilities to obtain special types of materials.

This is demonstrated here for preparation of hydrosodalite and BH_4 -sodalite filled steel mesh samples.

In the case of hydrosodalite, the space filling of the mesh was complete but a very close package was not reached. The strong hydrothermal leaching procedure of transformation of the hydroxysodalite into hydrosodalite was found to be responsible for the texture and packing density of the hydrosodalite crystals.

For BH_4 -sodalite, the space filling of the steel mesh is sufficient and shows a complete close and stable package. The structural directing effect of BH_4 -anions for the SOD structure type and the circumstance that no leaching procedure is needed to obtain BH_4 -sodalite seem to be the reasons for the better results compared with the hydrosodalite sample.

The investigation of the hydrosodalite transformation under insertion of an as synthesized pellet of hydroxysodalite without a steel mesh inlay revealed strong

damage like the formation of large pores within the hydrosodalite mould. These findings exclude a use as self-supported hydrosodalite membrane up to now. A further improvement of the self-supported hydrosodalite mould is necessary for future insertions. As a result of the zeolitic properties of hydrosodalite an increase of the efficiency of the membranes is highly expected compared with hydroxysodalite membranes. Investigations of the influence of pressure and time during pellet preparation and further optimization of heating parameters and leaching conditions after CS synthesis have to be performed in forthcoming studies. Further problems like evolution of pores as a result of the mechanically ripping out the steel inlay from the sample pellets after synthesis also have to be solved in future.

Nevertheless the results of the present paper are of significance for future improvement of wire mesh and self supported sodalite membranes.

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